

Supporting Information

1. Synthesis of **1**

1.1 Synthesis of 2-thienyl lithium

To a solution of 16mmol BuLi in 20 ml ether, cooled at $-70\text{ }^{\circ}\text{C}$, 2.60g (16mmol) 2-bromothiophene was added dropwise. The reaction was allowed to warm to room temperature and was stirred for 4 hours to give a solution of 14 mmol of 2-thienyl lithium in 20 ml ether

1.2 Synthesis of **1a**

To a solution of 14mmol of 2-thienyl lithium in 20 ml ether was added dropwise of 2.04 g (14mmol) of petamethylfulvene. The reaction mixture was stirred overnight. 1.52g (14mmol) of trimethylsilyl chloride in 10 ml THF was added dropwise. The mixture was stirred for 4h, and then poured into 100ml ice-water. The water layer was extracted with 30ml Et₂O, after which combined organic layers were rinsed with 100ml of brine. The organic phase was dried on MgSO₄. After the low-boiling volatiles were evaporated in vacuo, the residue was chromatographed (petroleum) to give **1a** in yield of 41% (1.7g).

1.3 Synthesis of **1**

To a solution of 0.50ml (4.6mmol) of TiCl₄ in 30 ml CH₂Cl₂, cooled to $-40\text{ }^{\circ}\text{C}$, was added dropwise a solution of 1.38g (4.6mmol) of **1a** in 10 ml CH₂Cl₂. The mixture was warmed to room temperature and stirred over night, The methylene chloride was remove in vacuo, and the residue was extracted with 1:3(v/v) mixture of CH₂Cl₂ and petroleum ether, and afforded a red crystals in 23% yield (400mg). ¹HNMR (500MHz, CDCl₃) δ 7.25 (m, 1H, α -Thiophene-H); δ 7.00 (m, 2H, β -Thiophene-H); δ 6.98 (pst, ³J_{HH}=2.9Hz, 2H, Cp-H); δ 6.79 (pst, ³J_{HH}=2.9Hz, 2H, Cp-H); δ 2.60 (d, ²J_{HH}=12.9Hz, 2H, α -CH_{eq}); δ 2.14 (m, 2H, α -CH_{ax}); δ 1.66 (br, 3H, β -and γ -CH₂); δ 1.27-1.54 (m, 3H, β -and γ -CH₂). Anal. C₁₅H₁₇Cl₃STi, found (calc) C: 47.28 (46.96) H: 4.49 (4.47).

2. Synthesis of **2**

2.1 Synthesis of 3-thienyl lithium

To a solution of 50mmol BuLi in 60 ml ether, cooled at $-70\text{ }^{\circ}\text{C}$, 8.15g (50mmol) 3-bromothiophene was added dropwise. The reaction was allowed to warm to room temperature and was stirred for 4 hours to give a solution of 46 mmol of 3-thienyl lithium in 60 ml ether

2.2 Synthesis of **2a**

To a solution of 23mmol of 3-thienyl lithium in 30 ml ether was added dropwise of 3.36 g (20mmol) of petamethylfulvene. The reaction mixture was stirred overnight. 2.50g (23mmol) of trimethylsilyl chloride in 10 ml THF was added dropwise. The mixture was stirred for 4h, and then poured into 100ml ice-water. The water layer was extracted with 30ml Et₂O, after which combined organic layers were rinsed with 100ml of brine. The organic phase was dried on MgSO₄. After the low-boiling volatiles were evaporated in vacuo, the residue was chromatographed (petroleum) to give **2a** in yield of 60% (4.0g).

2.3 Synthesis of **2**

To a solution of 0.54ml (5.0mmol) of TiCl₄ in 30 ml CH₂Cl₂, cooled to $-40\text{ }^{\circ}\text{C}$, was added dropwise a solution of 1.60g (5.0mmol) of **2a** in 10 ml CH₂Cl₂. The mixture was warmed to room temperature and stirred over night, The methylene chloride was remove in v acuo, and the residue was extracted with 1:3(v/v) mixture of CH₂Cl₂ and petroleum ether, and afforded **2** in 20% yield (380mg, yellow powder). ¹HNMR (500MHz, CDCl₃) δ 7.33 (dd, ²J_{HH}=5.0Hz, ³J_{HH}=2.9Hz, 1H, α -Thiophene-H); δ 7.19 (dd, ²J_{HH}=2.9Hz, ³J_{HH}=1.2Hz, 1H, α -Thiophene-H); δ 7.07(dd, ²J_{HH}=5.0Hz, ³J_{HH}=1.2Hz, 1H, β -Thiophene-H); δ 6.90 (pst, ³J_{HH}=2.9Hz, 2H, Cp-H); δ 6.78(pst, ³J_{HH}=2.8Hz, 2H, Cp-H); δ 2.59 (d, ²J_{HH}=12.9Hz, 2H, α -CH_{eq}); δ 2.03 (m, 2H, α -CH_{ax}); δ 1.53-1.70 (br, 3H, β -and γ -CH₂); δ 1.30-1.44 (m, 3H, β -and γ -CH₂). Anal. C₁₅H₁₇Cl₃STi, found (calc.) C: 47.00 (46.96) H: 4.61 (4.47).

3. Aparatus

¹HNMR spectra were recorded on Bruker AVANCE 500; EA was performed on EA-1106; GC was performed on Shimadazu-14B instrument equipped with a SE-30 column (30m \times 0.25mm) and a flame ionization detector; GC-MS analyses were conducted using a HP5973 mass-selective detector attached to a HP 6890 GC instrument.

4. General procedure for ethylene conversion:

A 100ml autoclave, equipped with a magnetic stirring bar, was preheated at 100 °C under vacuum for 30 min and then cooled to the required temperature. 20 ml toluene was injected into the reactor and pressured with ethylene. After equilibrating for 20 min, the appropriate volume of catalyst solution and MAO were injected to start the reaction. The ethylene pressure was kept constant during the reaction. After the desired run time, the reactor was vented and the reaction mixture was terminated by ethanol. n-Heptane was added to the mixture as internal standard for GC analysis. A clear solution was separated from the reaction mixture to analyze and quantify the soluble components by GC and GC-MS. The polymer was stirred in acidic ethanol for ten minutes, then rinsed with ethanol for several times and dried under vacuum.